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## Physical-Chemical Processes in a Protoplanetary Cloud

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### ABSTRACT

According to current views, the protosun and protoplanetary disk were formed during the collapse of a fragment of the cold, dense molecular interstellar cloud and subsequent accretion of its matter to a disk. One of the most critical cosmochemical issues in this regard is the identification of relics of such matter in the least altered bodies of the solar system: chondrites, comets, and interplanetary dust. The presence of deuterium-enriched, carbon-containing components in certain chondrites (Pillinger 1984) and radicals and ions in comets (Shulman 1987) is evidence that this area holds great promise. If a relationship is established between solar nebula and interstellar matter, we can then identify certain details, such as the interstellar cloud from which the Sun and the planets were formed. We can also come to a deeper understanding of the nature of physico-chemical processes in the protoplanetary cloud which yielded the tremendous diversity of the chemical and mineralogical compositions of the planets and their satellites, meteorites, and comets.

### CHARACTERISTICS OF THE CHEMICAL COMPOSITION OF MOLECULAR INTERSTELLAR CLOUDS

One would expect that chemical compositions of interstellar clouds are significantly varied and are a function of such physical parameters as temperature and density. Moreover, one would expect that they are also dependent on the age of a cloud, its history, the impoverishment of

elements, the flux of the energy particles of cosmic rays and photons, and the flow of material emanating from stars located in or adjacent to a cloud.

Several objects have been studied in the greatest detail at this time (Irvine *et al.* 1987): (1) The core of the KL region of the Orion nebula. It contains at least four identified subsources with varying chemistry. (2) The central galactic cloud Sgr B2. It is the most massive of all the known gigantic molecular clouds and contains high-luminosity stars. (3) The cold, dark, low-mass clouds, TMC-1 and L134N. They have substructures with individual "lumps" with a mass of several  $M_{\odot}$ . It has been suggested that such areas correspond to locations where solar-type stars were formed. TMC-1, in particular, matches that portion of ring material which is predicted by the rotating molecular cloud collapse model. (4) Clouds in the spiral arm. These are sources of HII areas or are the remnants of supernova CaSA. (5) The expanding envelope of the evolving carbon star, IRC + 10216 (CWLeO). Table 1 provides data on 80 molecules which were discovered by 1988 in the interstellar medium. Of these, 13 are new and three are the cyclical molecules,  $C_3H_2$ ,  $SiC_2$  and  $c-C_3H$ . A maximum high deuterium-enrichment  $D/H \approx 10^4 \times (D/H)_{cosm}$  (Bell *et al.* 1988) is characteristic for the first of these. The ratio  $[C_3HD]/[C_3H_2]$  lies within the range 0.05-0.15 for 12 dark, cold (approximately 10K) clouds. The first phosphorus compound (PN) discovered in the interstellar medium is among the new molecules. Phosphorus nitride has been discovered in three gigantic molecular clouds and, in particular, in the Orion nebula. In the Orion nebula it associates with dark gas flowing from the infrared source IRC2. This is most likely a protostar. PN abundance is low, while the search for other phosphorus compounds ( $PH_3$ ,  $HCP$ , and  $PO$ ) has yet to meet with success. This may seem strange, because P abundance in diffuse clouds approaches cosmic levels. However, many metals and S are impoverished because they are among the constituents of dust grains.

Data relating to the discovery of  $NaCl$ ,  $AlCl$ ,  $KCl$ , and  $AlF$  in envelopes of evolving stars are of tremendous interest. The carbon star IRC +10216 is an example. The distributions of these compounds are in agreement with calculations of chemical equilibria for the atmospheres of carbon-rich stars ( $C/O > 1$ ) in the area  $T = 1200-1500K$ . In addition to the molecules indicated above,  $SiH_4$ ,  $CH_4$ ,  $H_2C=CH_2$ ,  $CH=CH$ ,  $SiC_2$  have been discovered in the envelopes of stars. The latter molecule is particularly interesting: it broadens the range of molecules which condense at  $C/O > 1$ . Data on the search for  $O_2$  in six dark clouds are also evidence of the presence of dark clouds which characterize an oxygen insufficiency.

Two important consequences follow from the data contained in Table 1. (1) The obviously nonequilibrium nature of interstellar chemistry. Evidence of this is the presence of highly reactive ions and radicals with one or two unpaired electrons. (2) The presence of numerous molecules with

TABLE 1 Identification of Interstellar Molecules (Irvine 1988)

*Simple hydrides, oxides, sulfides and other molecules*

H <sub>2</sub>	CO	NH <sub>3</sub>	CS	<u>NaCl<sup>x</sup></u>
HCl	SiO	SiH <sub>4</sub> <sup>x</sup>	SiS	<u>AlCl<sup>x</sup></u>
H <sub>2</sub> O	SO <sub>2</sub>	CC	H <sub>2</sub> S	<u>KCl<sup>x</sup></u>
	OCS	CH <sub>4</sub> <sup>x</sup>	<u>PN</u>	<u>AlF<sup>x</sup></u>
	HNO ?			

*Nitriles, derivative acetylenes, and other molecules*

HCN	HC≡C-CN	H <sub>3</sub> C-C≡C-CN	H <sub>3</sub> C-CH <sub>2</sub> -CN	H <sub>2</sub> C=CH <sub>2</sub> <sup>x</sup>
H <sub>3</sub> CCN	H(C≡C) <sub>2</sub> -CN	H <sub>3</sub> C-C≡CH	H <sub>2</sub> C≡CH-CN	HC≡CH <sup>x</sup>
CCCO	H(C≡C) <sub>3</sub> -CN	H <sub>3</sub> C-(C≡C) <sub>2</sub> -H	HNC	
<u>CCCS</u>	H(C≡C) <sub>4</sub> -CN	H <sub>3</sub> C-(C≡C) <sub>2</sub> -CN?	HN=C=O	
HC=CCHO	H(C≡C) <sub>5</sub> -CN		HN=C=S	
<u>H<sub>3</sub>CNC</u>				

*Aldehydes, alcohols, ethers, ketones, amides, and other molecules*

H <sub>2</sub> C=O	H <sub>3</sub> COH	HO-CH=O	H <sub>2</sub> CNH
H <sub>2</sub> C=S	H <sub>3</sub> C-CH <sub>2</sub> -OH	H <sub>3</sub> C-O-CH=O	H <sub>3</sub> CNH <sub>2</sub>
H <sub>3</sub> C-CH=O	H <sub>3</sub> CSH	H <sub>3</sub> C-O-CH <sub>3</sub>	H <sub>2</sub> NCN
NH <sub>2</sub> -CH=O	<u>(CH<sub>3</sub>)<sub>2</sub>CO?</u>	H <sub>2</sub> C=C=O	

*Cyclical molecules*

C <sub>3</sub> H <sub>2</sub>	SiC <sub>2</sub> <sup>x</sup>	<u>c-C<sub>3</sub>H</u>
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*Ions*

CH <sup>+</sup>	HCO <sup>+</sup>	HCNH <sup>+</sup>	H <sub>3</sub> O <sup>+</sup> ?
HN <sub>2</sub> <sup>+</sup>	HOCO <sup>+</sup>	SO <sup>+</sup>	HOC <sup>+</sup> ?
	HCS <sup>+</sup>		H <sub>2</sub> D <sup>+</sup> ?

*Radicals*

OH	C <sub>3</sub> H	CN	HCO	<u>C<sub>2</sub>S</u>
CH	C <sub>4</sub> H	C <sub>3</sub> N	NO	NS
C <sub>2</sub> H	C <sub>5</sub> H	<u>H<sub>2</sub>CCN</u>	SO	
	<u>C<sub>2</sub>H</u>			

(a) New molecules discovered after 1986 are underlined.

(x) Present only in clouds of evolving stars.

(?) Not yet confirmed.

unsaturated bonds, despite the fact that hydrogen distribution rates are three to four orders greater than for C, N, and O. This is evidence of the predominance of kinetic over thermodynamic factors in chemical reactions in the interstellar medium and of the large contribution of energy from cosmic rays and UV radiation to these processes. Chemically saturated compounds such as  $\text{CH}_3\text{CH}_2\text{CN}$  are only present in the "warmer" sources (i.e., in Orion).  $\text{HNCO}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{HC}_3\text{N}$ ,  $\text{C}_2\text{H}_3\text{CN}$ ,  $\text{C}_2\text{H}_5\text{CN}$  levels are higher in warm clouds, possibly owing to higher  $\text{NH}_3$  parent molecule levels.

One interesting feature pertaining to the distribution rates for certain interstellar molecules is their uniformity for dark molecular clouds with wide variation in P and T parameters. Furthermore, an inverse dependence of the amount of gas molecules on dust density is absent. This would have been an expected consequence of molecules freezing into the ice mantle of particles. This is confirmed by data on the constancy of the CO/dust ratio in three clouds. It is further supported by the absence of a drop in  $\text{H}_2\text{CO}$  levels as dust density rises in dark molecular clouds. An indication that the efficiency rate of this in-freezing is not uniform for various molecules has also not been confirmed. A high degree of homogeneity of the  $\text{H}^{13}\text{CO}/^{13}\text{CO}$  and  $\text{C}_2\text{H}/^{13}\text{CO}$  ratios for many clouds has been found. Clearly, the processes involved in the breakdown of particle ice mantles are highly efficient. Their efficiency may be enhanced when dust grain density increases as the grains collide with each other.

Data on the distribution of different interstellar molecules are in general agreement with calculations in which ion-molecular reactions in gas are the primary process. However, there is a question as to the reliability of calculations with a value of  $\text{CO} < 1$  in a gas phase. It has been found that the abundance values for many C-rich molecules and ions are extremely low in steady-state conditions. Despite the fact that various explanations of these facts have been offered, an alternative hypothesis suggests that  $\text{C/O} > 1$  in the gas phase. Other facts were already indicated above which can be explained by such a composition of the gas phase. Enhanced carbon levels may be attributed to the fact that  $\text{CH}_4$  (being a nonpolar molecular) is more easily volatilized from the surface of the grain mantle than  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .

Therefore, we can hypothesize that in certain dark molecular clouds or in different portions of them, the gas phase has a C/O ratio which departs from the cosmic value. This is fundamentally critical to understanding the processes in the early solar system. It has been found that many unique minerals of enstatite chondrites (including enstatite, silicon-containing kamacite, nainingerite, oldgamite, osbornite, and carbon) could only have been formed during condensation from gas with  $\text{C/O} > 1$  (Petaev *et al.*

1986). SiC and other minerals, which were condensed in highly reducing conditions, have also been found in CM-type carbonaceous chondrites (Lavrukhina 1983).

### PROPERTIES AND PHYSICO-CHEMICAL PROCESS IN THE GENESIS OF INTERSTELLAR DUST GRAINS

According to current thinking (Voshchinnikov 1986), the total sum of molecules in a "dense," not-too-hot gaseous medium of complex molecular composition precipitates into a solid phase, thereby forming embryos of dust grains. These grains then begin to grow through accretion of other molecular compounds or atoms. The grains may in turn act as catalysts for reactions to form new types of molecules on their surface. A portion of these remains as particles, and the rest converts to the gaseous phase.

Laminated interstellar grains are formed in this manner. Their cores are made up of refractory silicate compounds, metal iron, and carbon. The grain mantle is formed from a mixture of ices of water, ammonia, methane, and other low-temperature compounds with varying admixtures. Atomic carbon may also be adsorbed on the mantle surface at the low temperatures of dark molecular clouds. These dust grains are often aspherical. Their size is approximately  $0.3 \mu\text{m}$ . Generation of the finest particles ( $\lesssim 0.01 \mu\text{m}$ ) also takes place. They have no mantle due to the increased temperature of these grains as a single photon is absorbed or a single molecule is formed. The dust grains are usually coalesced as a result of photoelectron emission and collisions with electrons and ions. Mean grain temperature is approximately 10 K.

The following data are evidence of the chemical composition of dust grains.

#### (1) IR- absorption band:

- $\lambda 3.1 \mu\text{m}$  – ice  $\text{H}_2\text{O}$  ( $\text{NH}_3$ ),
- $\lambda 9.7$  and  $18 \mu\text{m}$  - amorphous silicates,
- $\lambda 4.61$  and  $4.67 \mu\text{m}$  – molecules with the groups CN and CO,
- $\lambda 3.3 \div 35 \mu\text{m}$  – molecules with the groups  $\text{CH}_2$ - and  $-\text{CH}_3$ .

#### (2) Emission spectra:

- $\lambda 11.3 \mu\text{m}$  – SiC,
- $\lambda 30 \mu\text{m}$  – mixtures of MgS, CaS,  $\text{FeS}_2$ ,
- $\lambda 3.5 \mu\text{m}$  – formaldehyde ( $\text{H}_2\text{CO}$ ),

six emission bands with  $\lambda 3.28 \div 11.2 \mu\text{m}$  ÷ large organic molecules ( $N_C \sim 20$ )

(3)  $\lambda 2200\text{\AA}$  ÷ graphite (?), carbines ( $-\text{C}\equiv\text{C}-$ ), amorphous and glassy carbon.

According to current views, at least part of the interstellar molecules is formed from reactions on dust grain surfaces. At low-grain surface temperatures and moderately high gas temperatures, atoms and molecules coming into contact with the surface may adhere to it. Van-der-Vaals effects determine a minimum binding energy value. However, significantly high values are also possible with chemical binding. Migration along the grain surface of affixed atoms generates favorable conditions for molecule formation. A portion of the released binding energy ( $E_c$ ) of atoms in a molecule is taken up by the crystal grid of the grain surface. If the remaining portion of the molecule's energy is greater than  $E_c$ , the molecule "comes unglued" and is thrown into the gas phase. This process is accelerated when the dust grains are heated by cosmic rays.  $H_2$ ,  $CH_4$ ,  $NH_3$ , and  $H_2O$  molecules are formed in this manner. Since the binding energy of C, N, O, and other atoms is on the order of 800 K, they adhere to the grain surface where they enter into chemical reactions with hydrogen atoms. The aforementioned molecules are thus formed. Part of these then "comes unglued," such as the  $H_2$  molecule. A portion freezes to the grain surface. The temperatures at which molecules freeze are equal to (K):  $H_2 - 2.5$ ,  $N_2 - 13$ ,  $CO - 14$ ,  $CH_4 - 19$ ,  $NH_3 - 60$ , and  $H_2O - 92$ . Hence, the formation of the mantle of interstellar dust grains and certain molecules in the gaseous phase of dense, gas-dust clouds occurs contemporaneously.

Table 2 lists certain data on the characteristics of the basic physical and chemical processes involved in the formation and subsequent evolution of interstellar dust grains and the astrophysical objects in which these processes occur. With these data we can evaluate the nature of processes occurring in the protoplanetary cloud during the collapse and subsequent evolution of the Sun. These basic processes triggered: 1) the breakdown and vaporization of dust grains under the impact of shock waves at collapse and the accretion of primordial cloud matter onto the protoplanetary disk; 2) the collision of particles; and 3) particle irradiation by solar wind ions. The role of these processes varied at different distances from the protosun. Yet the main outcome of the processes is that organic, gas-phase molecules and the cores of dust grains (surrounded by a film of high-temperature polymer organic matter) are present throughout the entire volume of the disk. They are obvious primary-starting material for the formation of a great variety of organics which are observed in carbonaceous chondrites (Lavrukhina 1983). Dust grains at great distances from the protosun ( $R \gtrsim 2$  AU) will be screened from the impact of high temperatures and solar radiation. They will therefore remain fairly cold in order to conserve water and other volatile molecules in the mantle composition. Comets, obviously, contain such primary interstellar dust grains.

TABLE 2 Characteristics of the Basic Physico-Chemical Processes of Interstellar Dust Grain Genesis

Process	Parameters	Proposed Chemical Compounds or Processes	Astrophysical Objects
1. Condensation of high temperature embryos	T=1400-1280K	Amorphous silicates, mixes of oxides MgO, SiO, CaO, FeO, Fe, Ni-particles, SiC, carbines, graphite(?) amorphous & glassy carbon	1) Atmospheres of cold stars ( $10^{10}$ - $10^{11}$ cm <sup>-3</sup> ), 2) Planetary nebulae 3) Envelopes of novae and supernovae, 4) Envelopes of red giants
2. Formation of mantle on embryos	T=700-25K	FeS, H <sub>2</sub> O, NH <sub>3</sub> , H <sub>2</sub> O, CH <sub>4</sub> x H <sub>2</sub> O Solid clatrates Ar, Kr, Xe. Carbines	1) Upper layers of cold stars and interstellar space, 2) Dispersed matter of old planetary nebulae, 3) GMC <sup>(x)</sup> , 4) Old supernovae envelopes
3. Coalescence of fine particles with formation of "sleeve" pooling type particles	$\bar{t} \sim 10$ yrs	Ice with phenocrysts from silicates, metals graphite (?)	Turbulent gas of protostellar clouds
4. Destruction of dust grains (primarily in mantles)	Particle life-span: ice- ( $10^7$ - $5 \cdot 10^8$ ) years, silicate- ( $4 \cdot 10^8$ - $2 \cdot 10^{10}$ ) years	1) Collision of particles with $V > 20$ km-c <sup>-1</sup> , 2) Sublimation, 3) Physical and Chemical destruction, 4) Photodesorption	1) Envelopes of red giants and novae, 2) Shock waves from supernovae flash, 3) Irradiation by high velocity ions of stellar wind and by high energy cosmic rays in GMC <sup>(x)</sup> and planetary nebulae
5. Oxidation-reduction reactions on grain surface	Low-temperature Fe oxidation by monatomic oxygen	FeO, Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>	Diffusion interstellar medium
Formation of hydrides	T=2.5-5 K	FeH, FeH <sub>2</sub> , hydrides of transitional metals	Dark GMC <sup>(x)</sup> zones
6. Formation of envelopes and dust from solid organic compounds	Radiation polymerization of organic compounds with prebiological compounds T $\geq$ 4K on grains (PAC) with subsequent breakdown into fragments	Tolines, hexamethylentetramine, cellulose, complex organic or prebiological compounds	UV-radiation, cosmic rays, shock waves in GMC <sup>(x)</sup>

(x) Gigantic dark molecular interstellar clouds

## THE ISOTOPE COMPOSITION OF VOLATILES IN BODIES OF THE SOLAR SYSTEM

Investigation of the isotope composition of H, O, C, N, and the inert gases in meteorites, planets, and comets is extremely relevant as we attempt to understand the processes involved in the genesis of the preplanetary cloud. The majority of these elements had a high abundance in the interstellar gas and the gas-dust, initial protosolar cloud. Great variation in the isotope composition for various cosmic objects is also characteristic of these elements. Such variation has made it possible to refute outmoded views of the formation of the protosolar cloud from averaged interstellar material (Lavrukhina 1982; Shukolyukov 1988).

From detailed studies of meteorites, we have been able to discover a number of isotopically anomalous components and identify their carrier phases (Anders 1987). These studies have demonstrated that the protomatter of the solar system was isotopically heterogeneous. For example, examination of the hydrogen isotope has shown that objects of the solar system can be subdivided into three groups in terms of the hydrogen isotopy (Eberhardt *et al.* 1987). (1) Deuterium-poor interstellar hydrogen, protosolar gas, and the atmospheres of Jupiter and Saturn; (2) deuterium-rich interstellar molecules (HNC, HCN, and  $\text{HCO}^+$ ) of dark molecular clouds of Orion A; and (3) the atmospheres of Earth, Titanus, and Uranus, the water of Halley's comet, interplanetary dust, and certain chondrite fractions of Orgueil CI and Semarkona LL3 occupy an intermediary position. Clearly, the isotopic composition of hydrogen in these components is determined by the mixing of hydrogen from two sources: a deuterium-poor and a deuterium-rich source. A single gas reservoir is thus formed.

A similar situation has been found for oxygen. Two oxygen components have been discovered in meteorites: impoverished and enriched  $^{16}\text{O}$  of nucleogenetic origin (Lavrukhina 1980). The relative abundance of oxygen isotopes in chondrules tells us that chondrite chondrules of all chemical groups are convergent in relation to a single oxygen reservoir, characterized by the values  $\delta^{18}\text{O} = 3.6 \pm 0.2\text{‰}$  and  $\delta^{17}\text{O} = 1.7 \pm 0.2\text{‰}$  (Lavrukhina 1987; Clayton *et al.* 1983). They are similar to the corresponding values for Earth, the Moon, achondrites, pallasites, and mesosiderites. On the basis of these data and the dual-component, isotopic composition of nitrogen, carbon, and the inert gasses (Levskiy 1980; Anders 1987), workers have raised the idea that protosolar matter was formed from several sources. For example, two reservoirs of various nucleosynthesis are proposed that differ in terms of their isotopic composition and the degree of mass fractionization (Lavrukhina 1982; Levskiy 1980). Shukolyukov (1988) proposes three sources: ordinary interstellar gas; material injected into the solar system by



an explosion of an adjacent supernova; and interstellar dust made up of a mixture of different stages of stellar nucleosynthesis.

The presence of at least two sources of matter in protoplanetary matter may be evidence of the need to reconsider the hypothesis of the contemporaneous formation of the Sun and the protoplanetary cloud from a single fragment of a gigantic molecular interstellar cloud.

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